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DETERGENTS OR CLEANING AGENTS

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Abstract: The invention relates to detergents or cleaning agents that contain tensides and optionally other conventional ingredients as well as particles with a particle size of from 5 to 500 nm. The inventive detergents or cleaning agents impart to the surface to be cleaned temporary dirt-repellent properties.

This invention concerns a detergent or cleaning agent that contains surfactants and optionally other conventional components, an agent for cleaning hard surfaces, a clear rinse agent for use in machine dishwashing as well as a textile detergent.

The cleaning of substrates, i.e., both hard surfaces and textiles, has great importance both in the home and in the commercial field. For one thing the washing or cleaning operations have a hygienic basis, and in many cases there are also aesthetic reasons. The aesthetic reasons are particularly important in the case of transparent or smooth surfaces. For instance "dusty" glass, including window panes, and also porcelain surfaces at least partially lose their gloss.

It has been found in observations in nature that the surfaces of plants have soil-repellent properties, since dirt particles cannot remain deposited on these surfaces for a long time. In addition, such surfaces are capable of being cleaned by rain or moving water. This effect is due to the wax layers found on the surface, and in particular on their surface structure.

European Patent EP 0772 514 discloses a self-cleaning surface for objects that copies plants, which has an artificial surface structure of ridges and valleys and is characterized by the fact that the distance between the ridges is in the range from 5 to 200 μm and the height of the ridges is in the range from 5 to 100 μm and at least the ridges consist of hydrophobic polymers and durably hydrophobized materials and the ridges cannot be separated by water or water with detergents.

The surfaces disclosed in the prior art have a permanently present surface with a specific structure. These surfaces are unsuitable in the area of detergents or cleaning agents, since because of the large number of surfaces that are to be cleaned a permanent change in the manufacturing of these substrates would have to be considered. The present invention was based on the task of making available a detergent or cleaning agent that is capable of temporarily modifying the substrate to be cleaned so that the surface of the substrate to be cleaned is temporarily given soil-repellent properties.

It was surprisingly found that a surface can temporarily be given soil repellent properties if particles with a particle size from 5 to 500 nm are added to an agent that optionally contains, other conventional ingredients in addition to surfactants.

Temporary modification of the surface in the sense of this invention means that the effect can be maintained after a few, in particular up to 4, washing or cleaning cycles.

Accordingly, the object of this invention is a detergent or cleaning agent containing surfactants and optionally other conventional ingredients, which is characterized by the fact that it contains particles with a particle size from 5 to 500 nm.

The particles used in accordance with the invention are preferably water-insoluble or only slightly water-soluble particles, that remain on the cleaned substrate after the washing or cleaning operation. These particles in accordance with the invention have a particle size from 5 to 500 nm, preferably 5 to 250 nm. Because of the particle size, these particles are also characterized as nanoscale particles. Any insoluble solids that occur in said size distribution can be used as particles. Examples of suitable particles are any precipitated silica gels, aerogels, xerogels, $\text{Mg}(\text{OH})_2$, boehmite ($\text{Al}(\text{O})\text{OH}$), ZrO_2 , ZnO , CeO_2 , Fe_2O_3 , TiO_2 , TiN , hydroxylapatite, bentonite, hectorite, SiO_2 , CeO_2 , SnO_2 , In_2O_3 , SnO_2 , NgAl_2O_4 , HfO_2 , sols like SiO_2 sols, Al_2O_3 sols or TiO_2 sols, as well as any mixtures of the above.

The content of these nanoscale particles in the agents in accordance with the invention should be set so that the surface of the substrate to be cleaned is sufficiently covered. Preferably

the agents contain 0.01-35 wt%, especially preferably 0.01-20 wt%, and in particular at least 0.1 wt%, for example, 0.5-10 wt%, of the nanoscale particles, with respect to the ready-to-use agent.

Through the use of the nanoscale particles it is possible to increase the wettability of the substrates to be cleaned markedly. In many cases contact angles of 5 to 20° can be achieved, which means that water or oil droplets spread almost completely on the surface.

This is particularly advantageous since in this way uniform coverage of the wetted substrate by the liquid is guaranteed and residues cannot accumulate in the droplets and form visible spots after drying.

A further improvement can be achieved by modifying the surface of the nanoscale particle. This can take place, for example by means of conventional complexing agents, so that the precipitation of Ca or Mg salts can be prevented. These compounds can be applied in an amount such that they are contained in the ready-to-use agent in amounts from 1 to 8 wt%, preferably from 3.0 to 6.0 wt%, and especially 4.0 to 5.0 wt%, with respect to the ready-to-use agent. Usually they are found on the surface of the particles.

One preferred class of complexing agents consists of the phosphonates. These preferred compounds include, in particular, organophosphates such as 1-hydroxyethane-1,1-diphosphonic acid (HEDP), aminotri(methylenephosphonic acid) (ATMP), diethylenetriaminepenta(methylenephosphonic acid) (DTPMP or DETPMP) and 2-phosphonobutane-1,2,4-tricarboxylic acid (PBS-AM), which are used mostly in the form of their ammonium or alkali metal salts. The phosphonates are applied to the surface of the particles in an amount such that they are contained in the ready-to-use agent in amounts from 0.01 to 2.0 wt%, preferably 0.05 to 1.5 wt%, and especially from 0.1 to 1.0 wt%.

In addition, substances that complex heavy metals can be used as complexing agents. Suitable heavy metal complexing agents are, for example, ethylenediaminetetraacetic acid (EDTA) or nitrilotriacetic acid (NTA) in the form of the free acids or as alkali metal salts and derivatives of said acids as well as alkali metal salts of anionic polyelectrolytes like polymaleates and polysulfonates.

Other suitable complexing agents are low-molecular hydroxycarboxylic acids like citric acid, tartaric acid, malic acid, lactic acid or gluconic acid, or their salts, with citric acid or sodium citrate being particularly preferred.

The surface of the particles can be modified, for example, by simple stirring of a suspension of the particles with the complexing agent; the complexing agent becomes attached to the surface of the particles during the stirring.

It is obvious to the specialist that the total amount of complexing agent that is to be incorporated into the agents does not have to be applied to the nanoscale particles. It is also possible to incorporate these compounds directly, wholly or partially.

A further increase of the wettability can also be achieved through the addition of hydrophilizing agents. Examples of such hydrophilizing agents are mono- or polyhydric alcohols, alkanolamines or glycol ethers, provided they are miscible with water. Preferably, the hydrophilizing agents are selected from ethanol, n- or isopropanol, butanols, ethylene glycol methyl ether, ethylene glycol ethyl ether, ethylene glycol propyl ether, ethylene glycol mono-n-butyl ether, diethylene glycol methyl ether, diethylene glycol ethyl ether, propylene glycol methyl, ethyl or propyl ethers, dipropylene glycol monomethyl or ethyl ethers, diisopropylene glycol monomethyl or ethyl ethers, methoxy-, ethoxy- or butoxytriglycol, 1-butoxyethoxy-2-propanol, 3-methyl-3-methoxybutanol, propylene glycol t-butyl ether alcohols, especially C₁-C₄ alkanols, glycols, polyethylene glycols, preferably with a molecular weight between 100 and 100,000, especially between 200 and 10,000, and polyols like sorbitol and mannitol, as well as polyethylene glycol that is liquid at room temperature, carboxylic acid esters, polyvinyl alcohols, ethylene oxide/propylene oxide block copolymers as well as any mixtures of the above.

The agents in accordance with the invention can be in the form of liquids to gels or also in solid form.

If the agents are in liquid or gel form, they are as a rule aqueous preparations that optionally contain still other organic solvents that are miscible with water, as well as thickeners. Among the water-miscible organic solvents are, for example, the compounds indicated above as hydrophilizing agents. The preparation of liquid to gel preparations can take place continuously or batchwise by simple mixing of the components, optionally at elevated temperature.

To adjust the viscosity, one or more thickening systems can be added to a liquid composition in accordance with the invention. The viscosity of the compositions in accordance with the invention can be measured by conventional standard methods (for example the Brookfield viscosimeter RVD-VII at 20 rpm and 20°C, spindle 3) and they are preferably in the range from 100 to 5000 mPa·sec. Preferred compositions have viscosities from 200 to 4000 mPa·sec, where values between 400 and 2000 mPa·sec are especially preferred.

Suitable thickeners are usually polymer compounds. These substances, also called swelling agents, are mostly organic high-molecular substances, which absorb liquids, swell and finally convert to viscous true or colloidal solutions and derive from the group of natural polymers, modified natural polymers and completely synthetic polymers.

Polymers that derive from nature and are used as thickeners are, for example, agar agar, carrageen, traganth, gum arabic, alginates, pectins, polyoses, guar flour, carob flour, starches,

dextrins, xanthan, gelatins and casein. Modified natural substances derive above all from the group of the modified starches and celluloses; as examples one may mention here carboxymethylcellulose and other cellulose ethers, hydroxyethylcellulose and hydroxypropylcellulose as well as seed meal ethers.

On top of that it is possible to use surfactant thickeners, for example alkyl polyglycosides like C₈₋₁₀ alkyl polyglucoside (APG® 220, manufacturer: Cognis Deutschland GmbH), G₁₂₋₁₄ alkyl polyglucoside (APG® 600, manufacturer: Cognis Deutschland GmbH).

The agents in solid form include, for example, powders, compacted particles like granulates and molded articles (tablets). The individual forms can be produced by methods known from the prior art such as spray drying, granulation and compression molding.

The surfactants that are contained in accordance with the invention are preferably selected from among nonionic, anionic, amphoteric and cationic surfactants as well as any mixtures of them.

The surfactants are preferably present in an amount from 0.1 to 50 wt%, preferably from 0.1 to 35 wt% and especially from 0.1 to 25 wt%, with respect to the composition.

Preferably used as nonionic surfactants are alkoxyated, advantageously ethoxylated, in particular primary alcohols with preferably 8-18 C atoms and an average of 1-12 mol ethylene oxide (EO) per mol of alcohol, in which the alcohol residue can be linear or preferably methyl-branched in position 2 or can contain linear and methyl branched residues in a mixture as is usually the case in oxo alcohol residues. In particular, however, alcohol ethoxylates with linear residues from alcohols of natural origin with 12-18 C atoms, for example coconut, palm, tallow oil or oleyl alcohol, and an average of 2-8 EO per mol of alcohol are preferred. Among the preferred ethoxylated alcohols are, for example, C₁₂₋₁₄ alcohols with 3 EO to 7 EO, C₉₋₁₁ alcohols with 7 EO, C₁₃₋₁₅ alcohols with 3 EO, 5 EO, 7 EO or 8 EO, C₁₂₋₁₈ alcohols with 3 EO, 5 EO or 7 EO and mixtures of these, like mixtures of C₁₂₋₁₄ alcohol with 3 EO and C₁₂₋₁₈ alcohol with 7 EO. Said degrees of ethoxylation are statistical averages, which can for a particular product be a whole or fractional number. Preferred alcohol ethoxylates have a narrow homolog distribution (narrow range ethoxylates, NRE). In addition to these nonionic surfactants it is also possible to use fatty alcohols with more than 12 EO. Examples of these are tallow fatty alcohol with 14 EO, 25 EO, 30 EO or 40 EO. Also, nonionic surfactants that contain the EO and PO groups in the molecule together are usable in accordance with the invention. Here block copolymers with EO-PO block units or PO-EO block units can be used, as well as EO-PO-EO copolymers or PO-EO-PO copolymers. Of course mixed alkoxyated nonionic surfactants in which EO and PO units are not distributed blockwise but rather statistically can also be used. Such products can be produced through the simultaneous action of ethylene and propylene oxide on fatty alcohols.

Especially preferred examples of nonionic surfactants that produce a good flow behavior by water on hard surfaces are the fatty alcohol polyethylene glycol ethers, fatty alcohol polyethylene/polypropylene glycol ethers and mixed ethers that can optionally be end group blocked.

Examples of fatty alcohol polyethylene glycol ethers are ones of formula (I)



in which R^1 stands for a linear or branched alkyl and/or alkenyl residue with 6-22, preferably 12-18 carbon atoms and n stands for numbers from 1 to 5.

These substances are commercial products. Examples include addition products of an average of 2 or 4 ethylene oxides to industrial $C_{12/14}$ coco fatty alcohols (Dehydol® LS-2 or LS-4, Cognis Deutschland GmbH) or addition products of an average of 4 mol ethylene oxide to $C_{14/15}$ oxo alcohols (Dobanol® 45-4, Shell). The products can have conventional or narrow homolog distribution.

Fatty alcohol polyethylene/polypropylene glycol ethers are understood to be nonionic surfactants of formula (II),



in which R^2 stands for a linear or branched alkyl and/or alkenyl residue with 6-22, preferably 12-18 carbon atoms, n stands for numbers from 1 to 0 [sic] and m stands for numbers from 1 to 4.

These substances are also commercially available products. Typical examples are addition products of an average of 5 mol ethylene oxide and 4 mol propylene oxide to industrial $C_{12/14}$ coconut fatty alcohol (Dehydol® LS-54, Cognis Deutschland GmbH) or 6.4 mol ethylene oxide and 1.2 mol propylene oxide to industrial $C_{14/14}$ coconut fatty alcohol (Dobanol® LS-980, Cognis Deutschland GmbH).

Mixed ethers are understood to be end-group-blocked fatty alcohol polyglycol ethers of formula (III)



in which R^3 stands for a linear or branched alkyl and/or alkenyl residue with 6-22, preferably 12-18 carbon atoms, n_3 stands for numbers from 1 to 10, m_2 stands for 0 or numbers from 1 to 4 and R^4 stands for an alkyl residue with 1-4 carbon atoms or a benzyl residue.

Typical examples are mixed ethers of formula (III) in which R^3 stands for an industrial $C_{12/14}$ coconut alkyl residue, n_3 stands for 5 or 10, m_3 stands for 0 and R^4 stands for a butyl group (Dehypon® LS-54 or LS-104, Cognis Deutschland GmbH). The use of butyl or benzyl group blocked mixed ethers is particularly preferred for reasons of industrial application.

Hydroxyalkylpolyethylene glycol ethers are understood to be compounds of the general formula (IV)



in which

R^5 stands for hydrogen or a straight-chain alkyl residue with 1-16 C atoms,

R^6 stands for a straight-chain or branched alkyl residue with 4-8 C atoms,

R^7 stands for hydrogen or an alkyl residue with 1-16 C atoms, and

n_4 stands for a number from 7 to 30

with the stipulation that the total number of C atoms contained in R^5 and R^7 is 6-16.

In addition, alkyl glycosides of the general formula $\text{RO}(\text{G})_x$ in which R means a primary straight-chain or methyl branched, especially methyl branched in position 2, aliphatic residue with 8-22, preferably 12-18 C atoms and G is a symbol that stands for a glucose unit with 5 or 6 C atoms, preferably glucose, can also be used as additional nonionic surfactants. The degree of oligomerization x, which gives the distribution of monoglycosides and oligoglycosides, is any number between 1 and 10; preferably x is 1.2-1.4.

Another class of nonionic surfactants that are used in particular in the solid agents are alkoxyated, preferably ethoxylated or ethoxylated and propoxylated fatty acid alkyl esters, preferably with 1-4 carbon atoms in the alkyl chain.

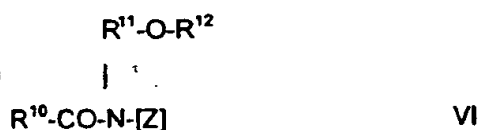
Also, nonionic surfactants of the type of the amine oxides, for example N-cocoalkyl-N,N-dimethylamine oxide and N-tallow alkyl-N,N-dihydroxyethylamine oxide, and the fatty acid alkanolamides can be suitable. The amount of these nonionic surfactants is preferably no more than that of the ethoxylated fatty alcohols, especially no more than half that amount.

Other suitable surfactants are polyhydroxy fatty acid amides of formula V,



in which R^8CO stands for an aliphatic residue with 6-22 carbon atoms, R^9 stands for hydrogen, an alkyl or hydroxyalkyl residue with 1-4 carbon atoms and $[\text{Z}]$ stands for a linear or branched polyhydroxyalkyl residue with 3-10 carbon atoms and 3-10 hydroxyl groups. The polyhydroxy fatty acid amides are known substances, which can conventionally be obtained by reductive amination of a reducing sugar with ammonia, an alkyl amine or an alkanol amine and subsequent acylation with a fatty acid, a fatty acid alkyl ester or a fatty acid chloride.

The group of the polyhydroxy fatty acid amides also includes compounds of formula VI,



in which R^{10} stands for a linear or branched alkyl or alkenyl residue with 7-12 carbon atoms, R^{11} stands for a linear, branched or cyclic alkyl residue or an aryl residue with 2-8 carbon atoms and R^{12} stands for a linear, branched or cyclic alkyl residue or an aryl residue or an oxyalkyl residue with 1-8 carbon atoms, where C_{1-4} alkyl or phenyl residues are preferred and $[\text{Z}]$ stands for a linear polyhydroxyalkyl residue, whose alkyl chain is substituted with at least two hydroxyl groups, or alkoxylated, preferably ethoxylated or propoxylated derivatives of these residues.

$[\text{Z}]$ is preferably obtained by reductive amination of a sugar, for example glucose, fructose, maltose, lactose, galactose, mannose or xylose. The N-alkoxy- or N-aryloxy-substituted compounds can then be converted to the desired polyhydroxy fatty acid amides by the reaction with fatty acid methyl esters in the presence of an alkoxide as catalyst, following the teaching of the International Application WO-A-95/07331.

Surfactants of the type of the sulfonates and sulfates, for example, are used as anionic surfactants. Possibilities as surfactants of sulfonate type here are preferably $\text{C}_{9/13}$ alkylbenzene sulfonates, olefin sulfonates, i.e., mixtures of alkene and hydroxyalkane sulfonates as well as disulfonates, such as are obtained, for example, from C_{12-18} monoolefins with terminal or internal double bond bisulfonation with gaseous sulfur trioxide followed by alkali or acid hydrolysis of the sulfonation products. Also suitable are alkanesulfonates, which are obtained from C_{12-18} alkanes, for example, by sulfochlorination or sulfoxidation followed by hydrolysis or neutralization. Likewise suitable are the esters of α -sulfofatty acids (ester sulfonates), for example the α -sulfonated methyl esters of hydrogenated coconut, palm kernel or tallow fatty acids.

The alkali and especially the sodium salts of sulfuric acid semiesters of C_{12} - C_{18} fatty alcohols, for example from coconut fatty alcohol, tallow fatty alcohol, lauryl, myristyl, cetyl or stearyl alcohol or the C_{10} - C_{20} oxo alcohols and the semiesters of secondary alcohols with these chain lengths are preferred as alk(en)yl sulfates. Additionally preferred are the alk(en)yl sulfates of said chain lengths that contain a synthetic petrochemically produced straight-chain alkyl residue. The C_{14} - C_{16} alkyl sulfates and C_{12} - C_{15} alkyl sulfates as well as C_{14} - C_{15} alkyl sulfates are preferred from the detergent standpoint. Also, 2,3-alkyl sulfates, which are preferably produced in accordance with US Patents 3,234,258 or 5,075,041 and can be obtained as commercial products from the Shell Oil Company under the trade name DAN® are suitable anionic surfactants.

Other suitable anionic surfactants are sulfonated fatty acid glycerol esters. Fatty acid glycerol esters are understood to be the mono-, di- and triesters as well as their mixtures, such as are obtained in manufacturing through the esterification of one monoglycerol with 1-3 mol fatty acid or in the transesterification of triglycerides with 0.3-2 mol glycerol. Preferred sulfonated fatty acid glycerol esters in this case are the sulfonation products of saturated fatty acids with 6-22 carbon atoms, for example caproic acid, caprylic acid, capric acid, myristic acid, lauric acid, palmitic acid, stearic acid or behenic acid.

Also, the sulfuric acid monoesters of straight-chain or branched C_7 - C_{21} alcohols that have been ethoxylated with 1-6 mol ethylene oxide, such as 2-methyl-branched C_{9-11} alcohols with an average of 3.5 mol ethylene oxide (EO) or C_{12-18} fatty alcohols with 1-4 EO, are suitable. They are used in cleaning agents only in relatively small amounts, for example in amounts from 1 to 5 wt%, because of their high foaming behavior.

Other suitable anionic surfactants are the salts of alkylsulfosuccinic acid, which are also called sulfosuccinates or sulfosuccinic acid esters and which are the monoesters and/or diesters of sulfosuccinic acid with alcohols, preferably fatty alcohols and especially ethoxylated fatty alcohols. Preferred sulfosuccinates contain C_{8-18} fatty alcohol residues or mixtures of them. Especially preferred sulfosuccinates contained a fatty alcohol residue that derives from ethoxylated fatty alcohols, which strictly speaking are nonionic surfactants (description, see below). Here again sulfosuccinates whose fatty alcohol residues derive from ethoxylated fatty alcohols with narrow homolog distribution are particularly preferred. Likewise, it is also possible to use alk(en)yl succinic acid with preferably 8-18 carbon atoms in the alk(en)yl chain or its salts.

Other anionic surfactants that are possibilities are in particular soaps, which are used especially in powdered agents and at higher pH values. Saturated and unsaturated fatty acid soaps such as the salts of lauric acid, myristic acid, palmitic acid, stearic acid, hydrogenated

erusic acid and behenic acid as well as soap mixtures that derive from natural fatty acids, for example coconut, palm kernel, olive oil or tallow fatty acids are suitable.

The anionic surfactants, including the soaps, can be in the form of their sodium, potassium or ammonium salts and as soluble salts of organic bases like mono-, di- or triethanolamine. Preferably the anionic surfactants are in the form of their sodium or potassium salts, especially in the form of the sodium salts.

Other surfactants that are possibilities are the so-called gemini surfactants. Among these are in general those compounds that have two hydrophilic groups and two hydrophobic groups per molecule. These groups, as a rule, are separated by a so-called "spacer." As a rule, the spacer is a carbon chain, which should be long enough that the hydrophilic groups have a sufficient spacing that they can react independently of each other. Such surfactants in general are characterized by unusually low critical micelle concentration and the ability to reduce the surface tension of water significantly. However, in exceptional cases the term gemini surfactants means not only dimer, but also trimer surfactants.

Suitable gemini surfactants are, for example, sulfated hydroxy mixed ethers of dimer alcohol bisulfates and trimer alcohol trissulfates and ether sulfates. End-group-blocked dimer and trimer mixed ethers are characterized particularly by their bi- and multifunctionality. Thus said end group blocked surfactants have good wetting properties and at the same time are low foaming, so that they are particularly suitable for use in machine washing or cleaning processes. However, gemini polyhydroxy fatty acid amides or poly-polyhydroxy fatty acid amides can also be used.

Examples of the cationic surfactants that can be used in the agents in accordance with the invention are in particular quaternary ammonium compounds. Ammonium halides like alkyltrimethylammonium chlorides, dialkyldimethylammonium chlorides and trialkylmethylammonium chlorides, for example cetyltrimethylammonium chloride, stearyl trimethylammonium chloride, distearyldimethylammonium chloride, lauryldimethylammonium chloride, lauryldimethylbenzylammonium chloride and tricetylmethylammonium chloride, are preferred. Other cationic surfactants that can be used in accordance with the invention are the quaternized protein hydrolyzates.

Likewise suitable in accordance with the invention are cationic silicone oils such as the commercially available products Q2-7224 (manufacturer: Dow Corning; a stabilized trimethylsilylamodimethicone), Dow Corning 929 emulsion (containing a hydroxylamino modified silicone, which is also called amodimethicone), SM-2059 (manufacturer: General Electric), SLM-55067 (manufacturer: Wacker) as well as Abil®-Quat 3270 and 3272 (manufacturer: Th. Goldschmidt; diquaternary polydimethylsiloxanes, Quaternium-80).

Alkylamidoamines, especially fatty acid amidoamines like the stearylamidopropyldimethylamine obtainable under the designation Tego Amid®S 18, are likewise usable and are characterized by their good biodegradability.

Likewise very highly biodegradable are quaternary ester compounds, the so-called "ester quats," such as the methylhydroxyalkyldialkyloxyalkylammonium methosulfates sold under the trade name Stepantex®.

An example of a quaternary sugar derivative that can be used as cationic surfactant is the commercial product Glucoquat®100, a "lauryl methyl gluceth-10 hydroxypropyl dimonium chloride," according to the CTFA nomenclature.

All of the builders that are usually used in detergents and cleaning agents can be contained in the detergent and cleaning agent molded articles in accordance with the invention, especially zeolites, silicates, carbonates, organic cobuilders and—where there are no ecological objections to their use—phosphates as well.

Suitable crystalline layer sodium silicates have the general formula $\text{NaMSi}_x\text{O}_{2x+1} \cdot \text{H}_2\text{O}$, where M means sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20 and preferred values for x are 2, 3 or 4. Preferred crystalline layer silicates of said formula are ones in which M stands for sodium and x takes on the values 2 or 3. Especially both β - as well as δ -sodium disilicates $\text{Na}_2\text{Si}_2\text{O}_5 \cdot y\text{H}_2\text{O}$ are preferred.

Also usable are amorphous sodium silicates with an $\text{Na}_2\text{O}:\text{SiO}_2$ ratio from 1:2 to 1:3.3, preferably from 1:2 to 1:2.8 and especially from 1:2 to 1:2.6, which are slow dissolving and have secondary detergent properties. The slow dissolving compared to traditional amorphous sodium silicates can be produced in various ways, for example by surface treatment, compounding, compaction/densification or by superdrying. Within the scope of this invention the term "amorphous" is also understood to mean "X-ray amorphous." This means that the silicates do not produce sharp X-ray reflections in X-ray diffraction experiments, as are typical for crystalline substances, but in any case give one or more peaks of the scattered X-ray radiation, which have a width of several degrees of the diffraction angle. However, particularly good builder properties can very probably result even if the silicate particles produce faded or even sharp diffraction peaks in electron diffraction experiments. One should interpret this to mean that the products have microcrystalline regions of magnitude 10 to a few hundred nm, where values up to a maximum of 50 nm and especially up to a maximum of 20 nm are preferred.

Densified/compacted amorphous silicates, compounded amorphous silicates and superdried X-ray amorphous silicates are especially preferred.

The finely crystalline synthetic zeolite, which contains bound water, that is used is preferably zeolite A and/or P. Zeolite MAP® (commercial product of the Crosfield) company is

particularly preferred as zeolite P. However, zeolite X as well as mixtures of A, X and/or P are also suitable.

Zeolites of the faujasite type may be mentioned as other preferably used and especially suitable zeolites. Together with zeolites X and Y the mineral faujasite belongs to the faujasite type within zeolite structural group 4, which is characterized by the double hexacycle subunit D6R (see Donald W. Breck: "Zeolite Molecular Sieves," John Wiley & Sons, New York, London, Sydney, Toronto, 1974, page 92). Besides said faujasite types the minerals chabazite and gmelinite as well as the synthetic zeolites R (chabazite type), S (gmelinite type), L and ZK-5 belong to zeolite structural group 4. The two last synthetic zeolites do not have any mineral analogs.

Zeolites of faujasite type are formed of β cages, which are joined tetrahedrally via D6R subunits, with the β cages being arranged similar to the carbon atoms in diamonds. The three-dimensional network of the zeolites of faujasite type that are used in the method in accordance with the invention has pores of 2.2 and 7.4 Å in size, the elementary cell moreover contains 8 cavities about 13 Å in diameter and can be described by the formula $\text{Na}_{86}[(\text{Al}_2)_{86}(\text{SiO}_2)_{106}] \cdot 264 \text{H}_2\text{O}$. The network of zeolite X then has a void volume of roughly 50%, with respect to the dehydrated crystal, which is the greatest empty volume of all of the known zeolites (zeolite Y: about 48% void volume, faujasite: about 47% void volume). (All data from: Donald W. Breck: "Zeolite Molecular Sieves," John Wiley & Sons, New York, London, Sydney, Toronto, 1974, pp. 145, 176, 177.)

Within the scope of this invention the term "zeolite of faujasite type" means all three zeolites that form the faujasite subgroup of the zeolite structural group 4. Besides zeolite X, zeolite Y and faujasite as well as mixtures of these compounds are usable in accordance with the invention, with the pure zeolite X being preferred.

Also, mixtures of cocrystallizates of zeolites of faujasite type with other zeolites, which do not necessarily belong to zeolite structural group 4, are usable in accordance with the invention, where the advantages of the process in accordance with the invention especially come to light in at least 50 wt% of the zeolites consists of zeolites of faujasite type.

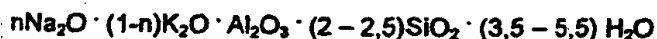
The aluminum silicates that can be used in the method in accordance with the invention are commercially available and the methods for their preparation are described in standard monographs.

Examples of commercially available zeolites of type X can be described by the following formulas:



in which x can take on values between 0 and 276 and which have pore sizes from 8.0 to 8.4 Å.

Commercially available and preferably usable within the scope of this invention is, for example, a cocrystallizate of zeolite X and zeolite A (about 80 wt% zeolite X), which is sold by the CONDEA Augusta S.p.A. under the trade name VEGOBOND AX® and which can be described by the formula



The zeolite can be used both as a builder in a granular compound and also for a kind of "powdering" of the overall mixture to the pressure molded, and usually both ways are used to incorporate the zeolite into the premix. Suitable zeolites have an average particle size of less than 10 µm (volume distribution; measurement method: Coulter counter) and preferably contain 18-22 wt%, especially 20-22 wt% bound water.

Of course it is also possible to use the generally known phosphates as builder substances, provided use of this kind should not be avoided for ecological reasons. Among the large number of commercially available phosphates the alkali metal phosphates have the greatest importance in the detergent and cleaning agent industry, with particular preference for pentasodium or pentapotassium triphosphate (sodium or potassium tripolyphosphate).

Alkali metal phosphates is the overall designation of the alkali metal (especially sodium and potassium) salts of the various phosphoric acids, within which metaphosphoric acids $(\text{HPO}_3)_n$ and orthophosphoric acid H_3PO_4 can be distinguished, in addition to the higher molecular representatives. The phosphates combine several advantages: they act as alkali carrier, they prevent calcium deposits on the machine parts or calcium encrustations in fabrics and, beyond that, they contribute to cleaning power.

Sodium dihydrogen phosphate, NaH_2PO_4 exists as the dihydrate (density 1.91 gcm^{-3} , melting point 60°C) and as the monohydrate (density 2.04 gcm^{-3}). Both salts are white powders that are very readily soluble in water, that lose the water of crystallization upon heating and that convert to the weakly acid diphosphate (disodium hydrogen diphosphate, $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$) at 200°C , to sodium trimetaphosphate ($\text{Na}_3\text{P}_3\text{O}_9$) and Maddrell salt at higher temperature (see below).

NaH_2PO_4 has an acid reaction; it is formed when phosphoric acid is adjusted to a pH of 4.5 with sodium hydroxide and the mixture is sprayed. Potassium dihydrogen phosphate (primary or monobasic potassium phosphate, potassium biphosphate, KDP), KH_2PO_4 , is a white salt with a density of 2.33 gcm^{-3} , has a melting point of 253°C (decomposition with the formation of potassium polyphosphate $(\text{KPO}_3)_x$) and is readily soluble in water.

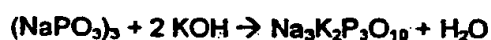
Disodium hydrogen phosphate (secondary sodium phosphate), Na_2HPO_4 , is a colorless, very readily water-soluble crystalline salt. It exists in water-free form and with 2 mol (density 2.066 gcm^{-3} , water loss at 95°C), 7 mol (density 1.68 gcm^{-3} , melting point 48°C with loss of 5 H_2O) and 12 mol of water (density 1.52 gcm^{-3} , melting point 35°C with loss of 5 H_2O), becomes water free at 100°C and converts to the diphosphate $\text{Na}_4\text{P}_2\text{O}_7$ with stronger heating. Disodium hydrogen phosphate is prepared by neutralizing phosphoric acid with a soda solution using phenolphthalein as indicator. Dipotassium hydrogen phosphate (secondary or dibasic potassium phosphate), K_2HPO_4 , is an amorphous white salt that is readily soluble in water.

Trisodium phosphate, tertiary sodium phosphate, Na_3PO_4 , consists of colorless crystals that as the dodecahydrate have a density of 1.62 gcm^{-3} and a melting point of $73\text{--}76^\circ\text{C}$ (decomposition), as the decahydrate (corresponding to 19-20% P_2O_5) has a melting point of 100°C and in water-free form (corresponding to 39-40% P_2O_5) has a density of 2.536 gcm^{-3} . Trisodium phosphate is readily soluble in water while having an alkaline reaction and is prepared by evaporating a solution of precisely 1 mol disodium phosphate and 1 mol NaOH . Tripotassium phosphate (tertiary or dibasic potassium phosphate), K_3PO_4 , is a white flowable granular powder with a density of 2.56 gcm^{-3} , has a melting point of 1340°C and is readily soluble in water, while having an alkaline reaction. It is formed, for example, in the heating of basic slag with coal and potassium sulfate. In spite of its high price, the more readily soluble and thus more highly effective potassium phosphates are in many cases preferred over the corresponding sodium compounds in the cleaning agent industry.

Tetrasodium diphosphate (sodium pyrophosphate), $\text{Na}_4\text{P}_2\text{O}_7$ exists in water-free form (density 2.534 gcm^{-3} , melting point 988°C , also given as 880°C) and as the decahydrate (density $1.815\text{--}1.836 \text{ gcm}^{-3}$, melting point 94°C with loss of water). Both substances are colorless crystals that are soluble in water with an alkaline reaction. $\text{Na}_4\text{P}_2\text{O}_7$ arises when disodium phosphate is heated to $>200^\circ\text{C}$ or is formed by reacting phosphoric acid with soda in a stoichiometric ratio and dehydrating the solution by spraying. The decahydrate complexes heavy metal salts and hardeners and thus reduces the hardness of the water. Potassium diphosphate (potassium pyrophosphate), $\text{K}_4\text{P}_2\text{O}_7$, exists in the form of the trihydrate and is a colorless hygroscopic powder with a density of 2.33 gcm^{-3} , which is soluble in water, and the pH of a 1% solution at 25°C is 10.4.

Higher molecular sodium and potassium phosphates in which one can identify cyclic representatives, sodium or potassium metaphosphates and chain types, sodium and potassium polyphosphates, are formed by condensation of NaH_2PO_4 or KH_2PO_4 . A large number of names are commonly used for potassium polyphosphates in particular: melt or thermal phosphates, Graham's salt, Kurrol's and Maddrell salt. All of the higher sodium and potassium phosphates are jointly called condensed phosphates.

The industrially important pentasodium triphosphate, $\text{Na}_5\text{P}_3\text{O}_{10}$ (sodium tripolyphosphate), is a nonhygroscopic white water-soluble salt of the general formula $\text{NaO}[\text{P}(\text{O})(\text{ONa})\text{O}]_n\text{Na}$ with $n = 3$, which is in water-free form or which crystallizes with 6 H_2O . About 17 g dissolves in 100 g water at room temperature, about 20 g at 60°C , around 32 g at 100°C for the crystallization water-free salt; after heating the solution to 100°C for 2 h about 8% orthophosphate and 15% diphosphate is formed by hydrolysis. In the preparation of pentasodium triphosphate phosphoric acid is reacted with a soda solution or sodium hydroxide solution in a stoichiometric ratio and the resulting solution is dehydrated by spraying. Like Graham's salt and sodium diphosphate, pentasodium triphosphate dissolves many insoluble metal compounds (also calcium soaps, etc.). Pentapotassium triphosphate, $\text{K}_5\text{P}_3\text{O}_{10}$ (potassium tripolyphosphate), is available, for example, in the form of a 50 wt% solution ($>23\%$ P_2O_5 , 25% K_2O). The potassium polyphosphates are widely used in the detergent and cleaning agent industry. In addition, there also exists sodium potassium tripolyphosphates, which are likewise usable within the scope of this invention. These substances arise, for example, if sodium trimetaphosphate is hydrolyzed with KOH :



These are usable in accordance with the invention exactly like sodium tripolyphosphate, potassium tripolyphosphate or mixtures of the two; also, mixtures of sodium tripolyphosphate and sodium potassium tripolyphosphate or mixtures of potassium tripolyphosphate and sodium potassium tripolyphosphate or mixtures of sodium tripolyphosphate and potassium tripolyphosphate and sodium potassium tripolyphosphate can be used in accordance with the invention.

In particular, polycarboxylates/polycarboxylic acids, polymer polycarboxylates, aspartic acid, polyacetals, dextrans, other organic cobuilders (see below) as well as phosphonates can be used as organic cobuilders. These substance classes are described below.

Usable organic builders are, for example, the polycarboxylic acids that are usable in the form of their sodium salts, where polycarboxylic acids are understood to mean carboxylic acids that have more than one acid function. For example, these include citric acid, adipic acid, succinic acid, glutaric acid, malic acid, tartaric acid, maleic acid, fumaric acid, sugar acids,

aminocarboxylic acids, nitrilotriacetic acid (NTA), provided there is no object to such use for ecological reasons, as well as mixtures of these substances. Preferred salts are the salts of the polycarboxylic acids like citric acid, adipic acid, succinic acid, glutaric acid, tartaric acid, sugar acids and mixtures of these.

The acids themselves can also be used. The acids typically have, besides their builder action, the properties of an acidifying component and thus also serve to establish a low and mild pH value in detergents and cleaning agents. In particular citric acid, succinic acid, glutaric acid, adipic acid, gluconic acid and any mixtures of these may be mentioned here.

In addition, polymer carboxylates are suitable as builders; these are, for example, the alkali metal salts of polyacrylic acid or polymethacrylic acid, for example ones with a relative molecular weight from 500 to 70,000 g/mol.

The molecular weights given for polymer polycarboxylates are within the sense of this document weight average molecular weights M_w for the relevant acid form, which were determined fundamentally using gel permeation chromatography (GPC), using a UV detector. The measurement in this case took place against an external polyacrylic acid standard, which because of its structural relationship to the tested polymers provides realistic molecular weight values. These data differ considerably from the molecular weight data in which polystyrene sulfonic acids are used as standard. The molecular weights measured against polystyrenesulfonic acids are as a rule considerably higher than the molecular weights given in this document.

Suitable polymers are in particular polyacrylates, which preferably have a molecular weight from 2000 to 20,000 g/mol. Again the short-chain polyacrylates, which have molecular weights from 2000 to 10,000 g/mol and especially preferably from 3000 to 5000 g/mol can be preferred from this group, because of their superior solubility.

Also suitable are copolymer polycarboxylates, especially those of acrylic acid with methacrylic acid and acrylic acid or methacrylic acid with maleic acid. Copolymers of acrylic acid with maleic acid that contain 50 to 90 wt% acrylic acid and 50 to 10 wt% maleic acid proved to be particularly suitable. Their relative molecular weight, with respect to the free acids, is in general 2000 to 70,000 g/mol, preferably 20,000 to 50,000 g/mol and especially 20,000 to 40,000 g/mol.

The (co)polymers polycarboxylates can be used either as powders or as aqueous solutions. The content of (co)polymer polycarboxylates in the agents is preferably 0.5-20 wt%, especially 3-10 wt%.

The polymers can also contain alkylsulfonic acids such as allyloxybenzenesulfonic acid and methallylsulfonic acid as monomer, in order to improve water solubility.

Also especially preferred are biodegradable polymers of more than two different monomer units, for example ones that contain as monomers salts of acrylic acid and maleic acid

as well as vinyl alcohol or vinyl alcohol derivatives or which contain as monomers salts of acrylic acid and 2-alkylallylsulfonic acid as well as sugar derivatives.

Other preferred copolymers are ones that exhibit preferably acrolein and acrylic acid/acrylic acid salts or acrolein and vinyl acetate as monomers.

One may likewise mention as other preferred builder substances polymer aminodicarboxylic acids, their salts or their precursors. Especially preferred are polyaspartic acids or their salts and derivatives.

Other suitable builder substances are polyacetals, which can be obtained by the reaction of dialdehydes with polyol carboxylic acids that have 5-7 C atoms and at least 3 hydroxyl groups. Preferred polyacetals are obtained from dialdehydes like glyoxal, glutaraldehyde, terephthalaldehyde as well as their mixtures and from polyolcarboxylic acids like gluconic acid and/or glucoheptonic acid.

Other suitable organic builders are dextrans, for example oligomers or polymers of carbohydrates, which can be obtained by partial hydrolysis of starches. The hydrolysis can be carried out by conventional processes, for example acid- or enzyme-catalyzed processes. Preferably, these are hydrolysis products with average molecular weights in the range from 400 to 500,000 g/mol. Here a polysaccharide with a dextrose equivalent (DE) in the range from 0.5 to 40, especially from 2 to 30, is preferred, where DE is a useful measure of the reducing action of a polysaccharide in comparison to dextrose, which has a DE of 100. Both maltodextrins with a DE between 3 and 20 and dry glucose syrups with a DE between 20 and 37 as well as the so-called yellow dextrans and white dextrans with higher molecular weights in the range from 2000 to 30,000 g/mol can be used.

The oxidized derivatives of such dextrans are their reaction products with oxidation agents that are capable of oxidizing at least one alcohol function of the saccharide ring to a carboxylic acid function. A product oxidized at C₆ of the saccharide ring can be particularly advantageous.

Oxydisuccinates and other derivatives of disuccinates, preferably ethylenediamine disuccinate, are also other suitable cobuilders. Here ethylenediamine N,N'-disuccinate (EDDS) is preferably used in the form of its sodium or magnesium salts. Also preferred in this connection are glycerol disuccinates and glycerol trisuccinates. Suitable amounts for use are 3-15 wt% in zeolite containing and/or silicate-containing formulations.

Other usable organic cobuilders are, for example, acetylated hydroxycarboxylic acids or their salts, which can also optionally be in lactone form and which contain at least 4 carbon atoms and at least one hydroxy group as well as a maximum of two acid groups.

The phosphonates are another class of substances with cobuilder properties. These are for the most part the same compounds that were listed above, such as hydroxyalkane or aminoalkane

phosphonates. Among the hydroxyalkane phosphonates 1-hydroxyethane 1,1-diphosphonate (HEDP) is of particular importance as a cobuilder. It is preferably used as the sodium salt; the disodium salt has a neutral reaction and the tetrasodium salt has an alkaline (pH 9) reaction. Preferably ethylenediamine tetramethylene phosphonate (EDTMP), diethylene triamine pentamethylene phosphonate (DTPMP) and their higher homologs are possibilities as aminoalkane phosphonates. They are preferably used in the form of the neutral sodium salts, for example as the hexasodium salt of EDTMP or as the heptasodium or octasodium salt of DTPMP. From the class of phosphonates HEDP is preferably used as builder. The amino alkane phosphonates additionally have a pronounced heavy metal binding capacity. Accordingly, it can be preferably, especially if the agents also contain bleach, to use aminoalkane phosphonates, especially DTPMP, or mixtures of said phosphonates.

Moreover, all of the compounds that are capable of forming complexes with alkaline earth ions can be used as cobuilders.

In addition, the agents in accordance with the invention can contain all of the substances that are usually contained in detergents and cleaning agents such as enzymes, bleaches, bleach activators, antiredeposition inhibitors, foam inhibitors, inorganic salts, solvents, pH adjusting agents, odorants, perfume vehicles, fluorescence agents, dyes, hydrotopes, silicone oils, soil release compounds, optical brighteners, antiredeposition inhibitors [sic], flow inhibitors, crease protection agents, dye transfer inhibitors, antimicrobial agents, germicides, fungicides, antioxidants, corrosion inhibitors, antistatic agents, ironing aids, water repellency and impregnation agents, antishrink and antislip agents, UV absorbers or their mixtures.

Possibilities as enzymes that can be used in the agents are one from the classes of the oxidases, proteases, lipases, cutinases, amylases, pullulanases, cellulases, hemicellulases, xylanases and peroxidases as well as their mixtures, for example proteases like BLAP®, Optimase®, Opticlean®, Maxacal®, Maxapem®, Alcalase®, Esperase® and/or Savinase®, amylases like Termamyl®, Amylase-LT®, Maxamyl®, Duramyl® and/or Purafect® OxAm, lipases like Lipolase®, Lipomax®, Lumafast® and/or Lipozyme®, cellulases likes Celluzyme® and/or Carezyme®. Particularly suitable are enzymatic active agents obtained from fungi or bacteria like *Bacillus subtilis*, *Bacillus licheniformis*, *Streptomyces griseus*, *Humicola lanuginosa*, *Humicola insolens*, *Pseudomonas pseudoalcaligenes* or *Pseudomonas cepacia*. The optionally used enzymes can as described, for example, in European Patent EP 0 564 476 or in the International Patent Applications WO 94/23005, be adsorbed on carrier substances and/or embedded in coating substances in order to protect them from premature inactivation. They are preferably contained in the surfactant mixtures in accordance with the invention in amounts up to 10 wt%, especially from 0.2 wt% to 2 wt%, where enzymes that are stabilized against oxidative degradation are especially preferred.

Among the compounds that serve as bleachers and produce H_2O_2 in water, sodium perborate tetrahydrate, sodium perborate monohydrate and sodium percarbonate are of particular importance. Other usable bleaches are, for example, persulfates and mixed salts with persulfates, such as the salts obtainable under the trade name CAROAT®, peroxy pyrophosphates, citrate perhydrates as well as H_2O_2 -producing peracid salts or peracids like perbenzoates, peroxophthalates, diperazelaic acid, diperdodecanoic acid or phthaloiminoperacids like phthaliminopercaproic acid. Organic peracids, alkali perborates and/or alkali percarbonates are preferably used, in amounts from 0.1 to 40 wt%, preferably 3-30 wt%, especially 5-25 wt%.

In the case of washing at temperatures of 60°C and below, and especially in laundry pretreatment to achieve an improved bleaching effect, bleach activators can be incorporated into the detergent and cleaning agent molded articles. Compounds that produce aliphatic peroxocarboxylic acids with preferably 1-10 C atoms, especially 2-4 C atoms, and/or optionally substituted perbenzoic acid, can be used as bleach activators. Substances that have the O- and/or N-acyl groups of said number of C atoms and/or optionally substituted benzoyl groups are suitable. Polyacylated alkylenediamines, especially tetraacetyleneethylenediamine (TAED), acylated triazine derivatives, especially 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine (DADHT), acylated glycolurils, especially 1,3,4,6-tetraacetylglycoluril (TAGU), N-acylimides, especially N-nonanoylsuccinimide (NASI), acylated phenolsulfonates, especially n-nonanoyl- or isononaoxyloxybenzensulfonate (n- or iso-NOBS), acylated hydroxycarboxylic acids like triethyl-O-acetyl citrate (TEOC), carboxylic anhydrides, especially phthalic anhydride, isatoic anhydride and/or succinic anhydride, carboxylic acid amides like N-methyldiacetamide, glycolide, acylated polyhydric alcohols, especially triacetin, ethylene glycol diacetate, isopropenyl acetate, 2,5-diacetoxy-2,5-dihydrofuran and the enol esters known from the German Patent Applications DE 196 16 693 and DE 196 16 767 as well as acylated sorbitol and mannitol or the mixtures described in the European Patent Application EP 0 525 239 (Sorman), acylated sugar derivatives, especially pentaacetyl glucose (PAG), pentaacetyl fructose, tetraacetyl xylose and octaacetyl lactose as well as acetylated, optionally N-alkylated glucamine or gluconolactone, triazole or triazole derivatives and/or particulate caprolactams and/or caprolactam derivatives, preferably N-acylated lactams, for example N-benzoylcaprolactam and N-acetylcaprolactam, which are known from the International Patent Applications WO-A-94/27970, WO-A-94/28102, WO-A-94/28103, WO-A-95/00626, WO-A-95/14759 and WO-A-95/17498, are suitable. The hydrophilically substituted acetals known from German Patent Application DE-A-196 16 769 and the acyllactams described in the German Patent Application DE-A-196 16770 and the International Patent Application WO-A-95/14075 are likewise preferably used. Also, the combinations of conventional bleach activators known from the German Patent Application DE-A-44 43 177 can be used. Nitrile derivatives like cyanopyridines, nitrile quats, for example

N-alkylammonium acetonitriles, and/or cyanamide derivatives can likewise be used. Preferred bleach activators are sodium 4-(octanoyloxy)benzenesulfonate, n-nonanoyl- or isononanoyloxybenzene sulfonate (n- or iso-NOBS), undecenoyloxybenzenesulfonate (UDOBS), sodium dodecanoyloxybenzenesulfonate (DOBS), decanoyloxybenzoic acid (DOBA, OBC 10) and/or dodecanoyloxybenzenesulfonate (OBS 12), as well as N-methylmorpholinium acetonitrile (MMA). Such bleach activators are contained in the usual ranges from 0.01 to 20 wt%, preferably in amounts from 0.1 to 15 wt%, especially 1 wt% to 10 wt%, with respect to the entire composition.

In addition to the conventional bleach activators or instead of them the agents can also contain the so-called bleach catalysts. These substances are bleach enhancing transition metal salts or transition metal complexes such as Mn, Fe, Co, Ru or Mo salen complexes or carbonyl complexes. Also, Mn, Fe, Co, Ru, Mo, Ti, V and Cu complexes with N-containing tripod ligands as well as Co, Fe, Cu and Ru ammine complexes are suitable as bleach catalysts, where preferably those compounds that are described in DE 197 09 284 A1 are used.

The detergents and cleaning agents in accordance with the invention are suitable both for cleaning hard surfaces including dishes as well as for washing textiles.

Accordingly, another object of this invention is an agent for cleaning hard surfaces that contains surfactants and particles with a particle size from 5 to 500 nm.

The cleaning of hard surfaces in the sense of this invention includes the cleaning of all surfaces that occur in the home and in the commercial area, including floors, walls and appliance surfaces as well as windows. The cleaning of dishes is also included. Steps for pretreatment and posttreatment, such as a rinse operation are also counted in the cleaning operation.

In one preferred embodiment an agent for cleaning hard surfaces in accordance with the invention contains 0.1-20 wt% particles with a particle size from 5-500 nm, 3-45 wt% surfactants, up to 10 wt% organic solvent (hydrophilizing agent), optionally complexing agents and water.

In one particularly preferred embodiment an agent for cleaning hard surfaces, especially for cleaning glass, contains 0.1-20 wt% particles with a particle size from 5 to 500 nm, up to 20 wt% water-soluble organic solvents, preferably ethanol or propanol, up to 10 wt% organic solvents, preferably glycol ether, 0.1-3 wt% nonionic surfactants, 0.1-3 wt% anionic surfactants, up to 2 wt% alkalizing agent, preferably ammonia or amines, optionally odorants and water.

Still another object of this invention is accordingly a textile detergent containing surfactants and particles with a particle size from 5 to 500 nm.

The textile detergents can be used, depending on their particular formulation, for laundry pretreatment, for laundry and for posttreatment, i.e., as a softener rinse.

In one preferred embodiment a textile detergent in accordance with the invention that is in solid form contains 0.1-35 wt% particles with a particle size from 5 to 500 nm, 2.5 wt% to 20 wt% anionic surfactant, 1 wt% to 20 wt% nonionic surfactant, 30 wt% to 55 wt% water-insoluble inorganic builders, up to 25 wt%, especially 1 wt% to 15 wt% bleach, up to 8 wt%, especially 0.5 wt% to 6 wt% bleach activator and up to 20 wt%, especially 0.1 wt% to 15 wt% inorganic salts, especially alkali carbonate, sulfate and/or silicate, and up to 2 wt%, especially 0.4 wt% to 1.2 wt% enzyme.

In a preferred embodiment a textile detergent in accordance with the invention that is in liquid form contains 0.1-32 wt% particles with particle size from 5 to 500 nm, up to 15 wt%, especially 3 wt% to 10 wt% anionic surfactants, up to 15 wt%, especially 3 wt% to 10 wt% nonionic surfactants, up to 18 wt%, especially 4 wt% to 16 wt% soap, 0.5 wt% up to 20 wt% water-soluble organic builders, up to 20 wt%, especially 0.1 wt% to 5 wt% water-insoluble inorganic builders, and up to 60 wt%, especially 10 wt% to 50 wt% water and/or water-miscible solvent, [no amount given] enzyme and up to 10 wt%, especially 0.01 wt% to 7.5 wt% enzyme stabilizer system.

Examples

Example 1: Glass cleaner

A. Glass cleaner formulations were prepared with the components listed in Table 1 by mixing the individual components.

Tests

A. Treatment of glass pane

The formulations were rubbed onto a glass pane and sprayed with dirty water (dispersion of water and a standard carpet soil). The test was conducted in comparison with an untreated glass pane and formulation without nanoparticles.

Result

The surface treated with nanoparticles showed a dirty water film that ran off uniformly. Large drops formed on the untreated surface and drops also remained on the surface polished with the glass cleaner. After drying the three glass panes were again compared. No soiling was seen on the surface treated with the nanoparticles, while clear soil residues could be seen as drop shaped spots on the other surfaces.

B. Methylene blue test

Process water was stained with methylene blue and applied to the glass panes pretreated as in A. The results are given in Table 2.

Table 1

Zusammensetzung / Gew.-% ①	② Beispiel							
	1	2	3	4	5	6	7	8
Ethanol	3,5	3,5	3,5	3,5	3,5	3,5	3,5	3,5
③ Ethylenglykolmonopropylether	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05
④ Alkylpolyglucosid (APG 220®)								
⑤ C ₁₂₋₁₈ -Fettalkoholethersulfat	0,3	0,3	0,1	0,3	0,3	0,3	0,1	0,1
⑥ Ammoniak	–	0,2	–	–	–	–	–	–
⑦ Duftstoff	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1
⑧ mit Milchsäure mod. Böhmit	–	–	0,9	1,0	–	–	–	–
⑨ Hectorit	–	–	–	–	2,6	–	–	–
⑩ Silicium(IV)-oxid-Sol® (wässrig, ca. 10%)	–	–	–	–	–	5,2	–	–
⑪ Aluminium-Sol® (wässrig, ca. 8%)	–	–	–	–	–	–	5,2	–
⑫ Titan(IV)-Sol® (wässrig, ca. 13 %)	–	–	–	–	–	–	–	5,2
⑬ Glycerin	–	–	2,2	–	3,8	–	–	–
⑭ Polyvinylalkohol	–	–	–	2,0	–	–	–	–
⑮ Citronensäure	–	–	–	–	–	5,0	–	–
⑯ Glucose	–	–	–	–	–	–	1,0	–
⑰ Sorbit	–	–	–	–	–	–	–	1,0
⑱ 1-Hydroxyethan-1,1-diphosphonsäure	–	–	–	–	0,1	0,1	–	–
⑲ Wasser	ad 100	ad 100	ad 100	ad 100	ad 100	ad 100	ad 100	ad 100

- Key:
- 1 Composition, wt%
 - 2 Example
 - 3 Ethylene glycol monopropyl ether
 - 4 Alkyl polyglucoside (APG 220®)
 - 5 C₁₂₋₁₈ fatty alcohol ether sulfate
 - 6 Ammonia
 - 7 Odorant
 - 8 Boehmite modified with lactic acid
 - 9 Hectorite
 - 10 Silicon(IV) oxide sol® (aqueous, about 10%)
 - 11 Aluminum sol® (aqueous, about 8%)

- 12 Titanium(IV) sol® (aqueous, about 13%)
 - 13 Glycerol
 - 14 Polyvinyl alcohol
 - 15 Citric acid
 - 16 Sorbitol
 - 17 1-Hydroxyethane-1,1-diphosphonic acid
 - 18 Water
- [ad = to]

C. Antifogging test

A glass surface treated with the formulation in accordance with the invention as in A and an untreated glass surface were held above steam. The results are given in Table 2.

Table 2

	① Beispiel							
Test-Methode ②	1	2	3	4	5	6	7	8
Methylenblau-Test ③	3	3	1	2	1	2	2	2
Antifogging-Test ④	6	6	1	1	1	1	1	1

Key: 1 Example
 2 Test method
 3 Methylene blue test
 4 Antifogging test

Evaluation criteria

Methylene blue test and long-term test

- 1 = closed water film with no edge run
- 2 = closed water film with slight edge run
- 3 = no hydrophilic effect

Antifogging test

- 1 = no fogging of pane
- 6 = complete fogging of pane

The test results show that in the methylene blue test a closed water film formed on the surface of the panes treated in accordance with the invention while in the comparison tests (Examples 1 and 2) a droplet pattern could be seen in addition to a pronounced edge run. In the

antifogging test no fog could be detected on the glass pane, in comparison with the untreated glass pane.

Overall the formulations in accordance with the invention that contain particles with a particle size from 5 to 500 nm show better wetting properties than the formulations without such properties.

Claims

1. A detergent or cleaning agent containing surfactants and optionally other conventional ingredients, which is characterized by the fact that it contains particles with a particle size from 5 to 500 nm.

2. A detergent or cleaning agent as in Claim 1, which is characterized by the fact that the particles have a particle size from 5 to 250 nm.

3. A detergent or cleaning agent as in one of Claims 1 or 2, which is characterized by the fact that the particles are selected from among any precipitated silica gels, aerogels, xerogels, $\text{Mg}(\text{OH})_2$, boehmite ($\text{Al}(\text{O})\text{OH}$), ZrO_2 , ZnO , CeO_2 , Fe_2O_3 , Fe_3O_4 , TiO_2 , TiN , hydroxylapatite, bentonites, hectorite, SiO_2 , CeO_2 , SnO_2 , In_2O_3 , SnO_2 , NgAl_2O_4 , HfO_2 , sols like SiO_2 sols, Al_2O_3 sols or TiO_2 sols as well as mixtures of the above.

4. Detergent or cleaning agents as in one of the Claims 1-3, which is characterized by the fact that the agents contain 0.01-35 wt% of the particles, with respect to the ready-to-use agent.

5. Detergents and/or cleaning agents as in one of Claims 1-4, which are characterized by the fact that the surfaces of the particles are modified with complexing agents selected from among the phosphonates like 1-hydroxyethane-1,1-diphosphonic acid, aminotri(methylenephosphonic acid), diethylenetriaminepenta(methylenephosphonic acid), as well as 2-phosphonobutane-1,2,4-tricarboxylic acid (PBS-AM), which are mostly in the form of their ammonium or alkali metal salts, heavy metal complexing agents like ethylenediamine tetraacetic acid or nitrilotriacetic acid in the form of the free acids or as alkali metal salts, their derivatives, alkali metal salts of anionic polyelectrolytes like polymaleates and polysulfonates, as well as low-molecular hydroxycarboxylic acids like citric acid, tartaric acid, malic acid, lactic acid or gluconic acid or their salts.

6. A detergent or cleaning agent as in one of Claims 1-5, which is characterized by the fact that it contains a hydrophilizing agent selected from the group consisting of ethanol, n-propanol or isopropanol, butanols, ethylene glycol methyl ether, ethylene glycol ethyl ether, ethylene glycol propyl ether, ethylene glycol mono-n-butyl ether, diethylene glycol methyl ether, diethylene glycol ethyl ether, propylene glycol methyl, ethyl or propyl ether, dipropylene glycol monomethyl or ethyl ether, diisopropylene glycol monomethyl or ethyl ether, methoxy, ethoxy or butoxy triglycol, 1-butoxyethoxy-2-propanol, 3-methyl-3-methoxybutanol, propylene glycol

t-butyl ether alcohols, especially C_1 - C_4 alkanols, glycols and polyols and polyethylene glycol that is liquid at room temperature, carboxylic acid esters and any mixtures of the above.

7. Detergents or cleaning agents as in one of Claims 1-6, which are characterized by the fact that they are in liquid or gel form or in solid form, in particular as powders or compacted materials like tablets.

8. Detergents or cleaning agents as in one of Claims 1-7, which are characterized by the fact that the surfactants are selected from among nonionic, anionic, amphoteric and cationic surfactants as well as any mixtures of them.

9. Detergents or cleaning agents as in one of Claims 1-8, which is characterized by the fact that builders selected from the group consisting of the zeolites, silicates, carbonates, organic builders and cobuilders and phosphates are contained in them.

10. Detergents or cleaning agents according as in one of Claims 1-9, which are characterized by the fact that they contain enzymes, bleaches, bleach activators, antiredeposition agents, foam inhibitors, inorganic salts, solvents, pH adjusting agents, odorants, perfume vehicles, fluorescence agents, dyes, hydrotopes, silicone oils, soil release compounds, optical brighteners, antiredeposition inhibitors, flow inhibitors, crease protection agents, color transfer inhibitors, antimicrobial agents, germicides, fungicides, antioxidants, corrosion inhibitors, antistatic agents, ironing aids, water repellent and impregnation aids, antismelling and antislip agents, UV absorbers or their mixtures.

11. Agents for cleaning hard surfaces containing surfactants and particles with a particle size from 5 to 500 nm.

12. Textile detergents containing surfactants and particles with a particle size from 5 to 500 nm.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 00/10393

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C11D17/00 C11D3/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 968 445 A (AHMED FAHIM U ET AL) 6 November 1990 (1990-11-06) claim 1; examples	1-4,7-11
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-/-		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"A" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

International Application No

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